A Tenative Identification of Average Aromatic Ring Size in an Iowa Vitrain and a Virginia Vitrain

B. C. Gerstein, L. M. Ryan, and P. Dubois Murphy

Ames Laboratory, U. S. Department of Energy, and
Department of Chemistry, Iowa State University
Ames, Iowa 50011

Introduction

A knowledge of the average aromatic ring size in coals is useful not only in indicating the appropriate chemistry one might use for conversion to fuel oil, but also as an indicator of possible physiological effects of contact with coals and coal products. In principle, NMR offers the capability of a direct determination of average ring size via an identification of the fractions of ^{13}C and ^{1}H in coals. Three factors prevent use of conventional NMR for this purpose in solid coals. The first is the effect of homonuclear and heteronuclear dipolar interactions which lead to linewidths of hundreds of ppm for both ^{1}H and ^{13}C in solid coals[1a,b]. The second is the fact that even in the absence of dipolar broadening, chemical shift anisotropies of ^{1}H can be as large as 34 ppm[2] for, e.g. the single species ^{1}H in $H_2O(s)$, such that a randomly oriented solid sample containing many protons in different chemical environments would exhibit an NMR spectrum in which individual protons could not be easily identified. A similar statement applies to NMR spectra of ^{13}C in solids. A third factor peculiar to coals is the possibility of an enormous number of chemically shifted species of a given nucleus, leading to NMR spectra which are still severely overlapping in the absence of broadening due to dipolar and chemical shift interactions.

In the present work, cross polarization to enhance sensitivity[3] combined with strong heteronuclear decoupling[4] and magic angle spinning[5] to remove heteronuclear dipolar broadening and chemical shift anisotropy broadening are used to distinguish aliphatic from aromatic ^{13}C in Pocahontas #4 vitrain, and Star vitrain. Combined rotation and multiple pulse (NMR) spectroscopy (CRAMPS)[6] are similarly used to narrow NMR spectra of ^{1}H in these coals. The ratios of aliphatic to aromatic ^{1}H and ^{13}C thus inferred are used to estimate an average aromatic ring size in the samples investigated.

Experimental

The NMR spectrometer used for determinations of spectra of both ^{1}H and ^{13}C has previously been described,[1a] as have the probes used for magic angle spinning[7, 8]. The Virginia coal "Pocahontas #4" was supplied by H. L. Retcofsky of the Pittsburgh Energy Research center of the U. S. Department of Energy. A vitrain portion of the Iowa coal "Star" was supplied by Dr. D. L. Biggs of the Iowa State University Department of Earth Sciences and the Ames Laboratory of the U. S. Department of Energy. The coals were analyzed for major constituents and free radical content as previously reported.[1] Results of these analyses are given in Table I.

Results

The high resolution solid state spectra of ^{13}C in both coals are shown in Figure 1. The high resolution solid state spectrum of ^{1}H in 2,6 dimethylbenzoic acid is shown in Figure 2, as an indication of the resolution available with equipment used in the present experiments. The high resolution solid state spectra of ^{1}H in both coals are

shown in Figures 3 and 4. Also indicated in Figures 2 - 4 are the Lorentzian
lines used to approximate the total experimental spectra, indicated by crosses
(+), and the sum of these lines indicated by the smooth curve through the
experimental points.

The mole ratios of aromatic hydrogen to aromatic carbon implied by the
elemental analyses given in Table I, and the fractions of aromatic to total hydrogen
and carbon calculated from the results of estimating the integrated areas
associated with these species as shown in Figures 2 - 4 yield the following
values for (H_{Ar}/C_{Ar}): Pocahontas #4, 0.53; Star, 0.40. At first thought, these
numbers seem a bit surprising, because Pocahontas, having the higher carbon content,
is an older coal, and one would expect a larger ring size to correspond to the
more "graphitized" material. A bit of reflection, as illustrated by the entries
in Table II, might help to remove the ambiguity.

TABLE I

Elemental analyses, Wt% (maf), free radical concentration, and fractions
of aromatic hydrogen and carbon.

SAMPLE	% C	%H	%N	%S	$[e^{\cdot}]$, spins g^{-1} x10^{-19} [a]	f_C^{Ar}	f_H^{Ar}
Pocahontas #4 Vitrain	90.3(2)	4.43(4)	1.28	0.85	4	0.86	0.77
Star Vitrain	77.0(1)	6.04(4)	1.17(14)	5.02	1.6	0.71	0.31

[a] Determination made on unheated sample

Table II

Average aromatic ring size as a function of H_{Ar}/C_{Ar} and connectivity

0.83   0.70   0.54   0.42   0.35

0.67

0.60   0.50

0.46

0.40

0.41

91
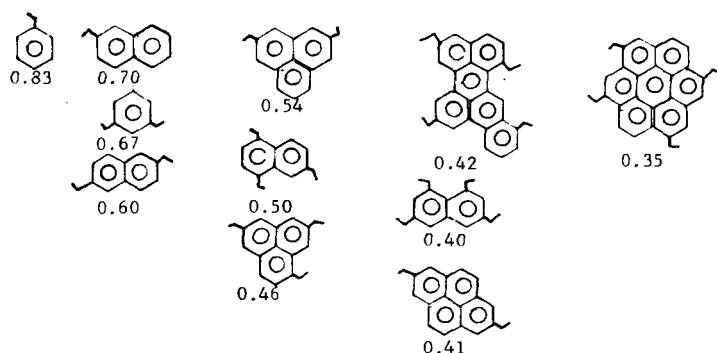
The point to be made from Table II is that the average aromatic ring size inferred from the aromatic hydrogen to carbon ratios depends a good deal upon the number of side chains, or functional groups, indicated by the symbol $\wedge$ in Table II , connected to the ring in question. We see that a value of 0.53 for this ratio is not inconsistent with an average ring size of three, with two connections per polyaromatic ring. On the other hand, a value of 0.40 is not inconsistent with an average ring size of two, with four connections per polyaromatic ring (but is also not in disagreement with an average ring size of four to six, as indicated in the fourth column of Table II). Our present prejudice is that the average polyaromatic hydrocarbon ring size in the older coal should be greater than that in the younger. With what we feel are reasonable values for connectivities, we thus infer that the average polyaromatic hydrocarbon ring size in Pocahontas #4 is no greater than three, and that in Star no greater than two, the values thus inferred being dependent upon the assumption that on the average, the younger coal has more aliphatic chains attached to the rings. Inference from ^{13}C spectra alone yield similar values[9].

One source of error in the above inferences is the fraction aromatic carbon, since it is known that not all carbon are polarized in cross polarization experiments[10]. A second most obvious source of error is the accuracy of resolving the high resolution solid state spectra of protons in these coals. The former error would tend to increase the ring size on the average, since it is quite probable that the carbons not seen in cross polarization experiments are in the neighborhood of stable free radicals, characterized by relatively large polyaromatic hydrocarbon rings. Relaxation times of protons under the spin locking conditions of the cross polarization experiments[11] may be sufficiently short to obviate effective cross polarization. Spin counting of protons with, and without strong homonuclear decoupling indicates that at least 95% of the protons in the present samples are being detected under the high resolution solid state techniques used in the present work.

92

Figure 1.

Figure 2.

^{1}H in POCAHONTAS #4 VITRAIN
CRAMPS @ $t_c = 36 \, \mu$ sec,
$f_{rot} = 2.5$ KHz

$f_{Ar} = 0.77$

Figure 3.

^{1}H in STAR VITRAIN
CRAMPS @ $t_c = 36$ u sec
$f_{rot} = 2.5$ KHz
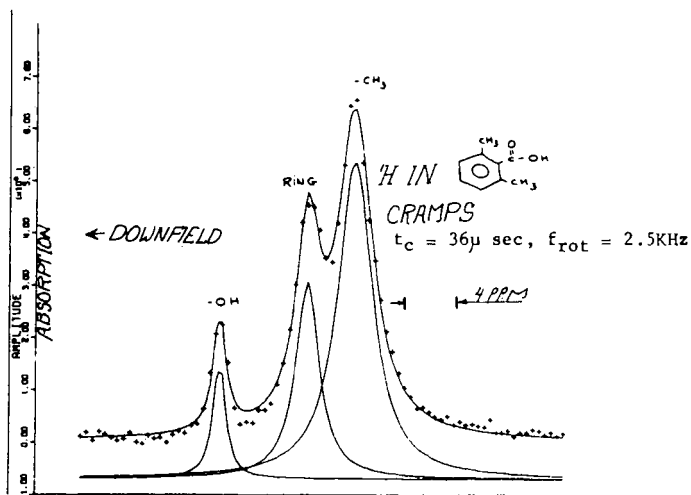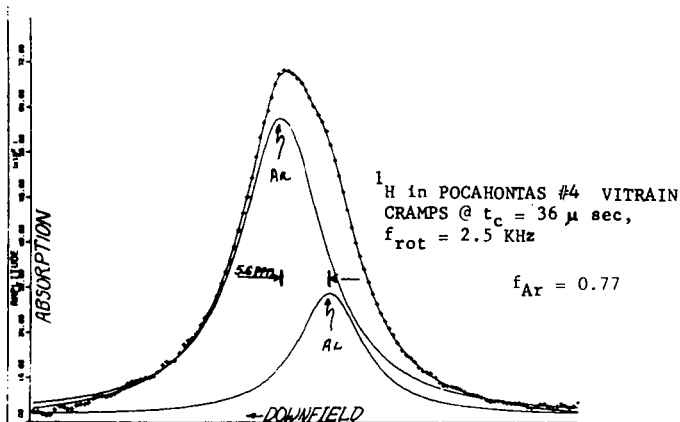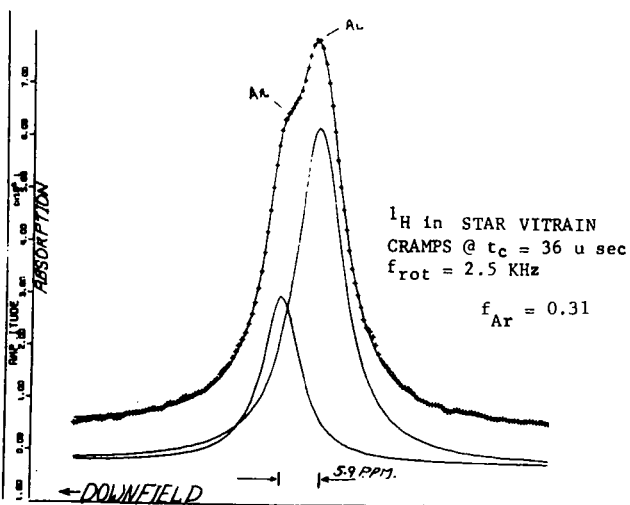
$f_{Ar} = 0.31$
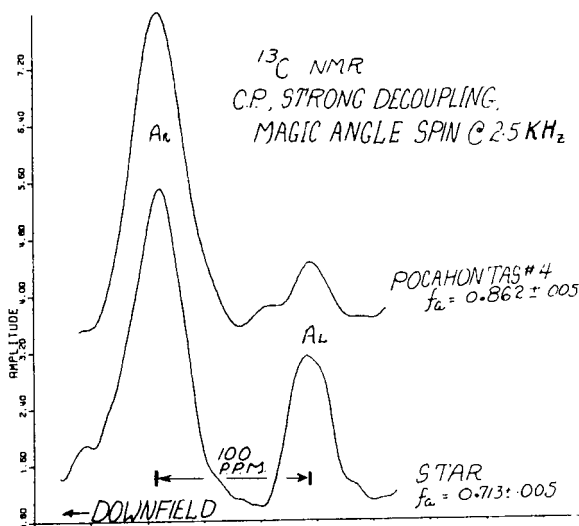
Figure 4.

94

References

1. a) B. C. Gerstein, C. Chow, R. G. Pembleton, and R. C. Wilson, J. Phys. Chem. $\underline{81}$, 565-70 (1977).

   b) H. L. Retcofsky and R. A. Friedel, J. Phys. Chem. $\underline{77}$, 68-71 (1973)

2. L. M. Ryan, R. C. Wilson, and B. C. Gerstein, Chem. Phys. Lett. $\underline{52}$, 341-4 (1977).

3. S. R. Hartman and E. L. Hahn, Phys. Rev. $\underline{128}$, 2042-53 (1962).

4. A. Pines, M. G. Gibby, and J. S. Waugh, J. Chem. Phys. $\underline{59}$, 569-95 (1973)

5. E. R. Andrew, in "Progress in Nuclear Magnetic Resonance Spectroscopy" Vol. 8, Part 1, Ed. J. W. Emsley, J. Feeney, and L. H. Sutcliff, Pergamon Press (1971).

6. B. C. Gerstein, R. G. Pembleton, R. L. Wilson, and L. M. Ryan, J. Chem. Phys. $\underline{66}$, 361-2 (1977).

7. R. G. Pembleton, L. M. Ryan, and B. C. Gerstein, Rev. Sci. Instr. $\underline{48}$, 1286-9 (1977).

8. P. D. Murphy and B. C. Gerstein, Report #IS-4388, Iowa State University, (1978).

9. H. L. Retcofsky and D. L. VanderHart, Fuel $\underline{57}$, 421 (1978).

10. D. L. VanderHart and H. L. Retcofsky, Fuel $\underline{55}$, 202 (1976).

11. B. C. Gerstein "Fingerprinting Solid Coals Using Pulse and Multiple Pulse Nuclear Magnetic Resonance", Chapter 52, in Vol 3, Analytical Methods for Coal and Coal Products , Ed. Clarence Karr, Jr., Academic Press (circa 1979).